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TRACE INORGANIC ELEMENT AND PARTICULATE
DEPOSITION MODEL - PART I

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ABSTRACT

First of two reports which will examine the dispersion and deposition of trace inorganic elements and particulates emitted from coal-fired power plants. The chemical species, range of particle sizes, their distribution in the waste products of coal combustion and wet and dry deposition from the atmosphere are examined. Part II will present the development of a trace inorganic element and particulate dispersion and deposition model.

INTRODUCTION

Coal, as a result of its geological origins, contains essentially all known stable chemical elements. Most inorganic elements, except for the abundant rock forming species oxygen (O), silicon (Si), aluminum (Al), iron (Fe), calcium (Ca), sodium (Na), potassium (K) and magnesium (Mg), are present in coal in only trace amounts. A compound is considered to be a trace element of coal if it is present at concentrations of less than 0.1% by weight (100 ppm) or less than 1000 ppm in ash/1/. During combustion, the carbon matrix is burned away and the mineral matter, in the form of clays, shales, sulfides, carbonates, chlorides, etc, is exposed to temperatures of 1500-1700°C. (The temperature of the combustion system varies according to the type of boiler, eg, pulverized dry bottom, pulverized wet bottom, cyclone, stoker). At these temperatures, most of the nonvolatile mineral matter fuses and highly spherical particles having the composition of amorphous mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) are formed. These particules serve as surfaces for the condensation or adsorption of the other inorganic

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species which are volatilized during coal combustion, ie, trace metals. Coal typically contains 2-30% noncombustible mineral material and as a result enormous quantities of ash (particulate matter) are produced in power generation/2/. The concentration of trace elements condensed on the surface of these aerosol particles can become very high. Most of the noncombustible material remains in the furnace as boiler slag and bottom ash. Some, however, passes into the flue gas stream as fly ash, a fraction of which is eventually emitted to the atmosphere. Even with the use of electrostatic precipitators or wet scrubbers, which operate at efficiencies of over 99%, considerable amounts of particulate matter escape from the stacks. Emission control devices are not successful at retaining smaller particulates, ie, less than 1 μm in diameter. As a result, urban aerosols can be enriched in trace elements by as much as 100 to 1000 fold over their natural crustal abundance. Trace element concentrations can become so high as to constitute a danger to the environment. Fine aerosol particles (<10 μm in diameter) adsorb the highest concentration of trace elements and are potentially hazardous to health because they penetrate deep into the lungs. The biogenic availability of trace elements concentrated on the surfaces of ash particles is expected to be greater than if the elements were distributed in the silicate matrix.

Many previous reports by Ontario Hydro's Research Division have examined trace inorganic elements in coal/3,4/. Attempts have been made to identify the elements and define their relative distribution in the waste products of coal combustion, eg, bottom ash, fly ash, flue gas. Little information about where and how the elements are removed from the troposphere is given. The negative environmental consequences of trace inorganic element emissions necessitates an understanding of these aspects and development of a model to describe trace element dispersion and deposition. Development/selection of a trace inorganic element and particulate dispersion and deposition model requires:

- (i) identification of the chemical and physical forms of the trace inorganic element and particulate emissions;
- (ii) an understanding of the dispersion process; and
- (iii) an examination of the wet and dry removal processes.

Topics (i) and (iii) will be addressed in the following. Using this information, a model capable of describing trace inorganic element and particulate dispersion and deposition in the range of up to 50 km and for averaging times of 1-10 y will be developed. The development or selection of a dispersion and deposition model from those available in the literature will be described in Part II.

CHEMICAL AND PHYSICAL FORMS OF THE TRACE INORGANIC ELEMENT EMISSIONS

Almost all elements in the Periodic Table have been detected in coal. The inorganic composition of coal varies considerably between mines and even within a seam/5/. Table I presents a list of the concentrations of the trace inorganic elements most commonly detected in US coals.

TABLE I
CONCENTRATION OF ELEMENTS IN
SOME USA COALS/5/

Element		Arithmetic mean	Standard deviation	Range of values	
				Min.	Max.
Ag	Silver	0.19ppm	0.24	< 0.03	0.80
As	Arsenic	14.02ppm	17.70	0.50	93.00
Au	Gold	0.01ppm	0.01	< 0.0006	0.032
Ba	Barium	130. ppm	150.	33.	750.
Be	Beryllium	1.61ppm	0.82	0.20	4.00
Ce	Cerium	11. ppm	4.3	4.4	24.
Cd	Cadmium	2.52ppm	7.60	0.10	65.00
Co	Cobalt	9.57ppm	7.26	1.00	43.00
Cr	Chromium	13.75ppm	7.26	4.00	54.00
Cs	Caesium	1.0 ppm	0.26	0.49	1.5
Cu	Copper	15.16ppm	8.12	5.00	61.00
Dy	Dysprosium	0.99ppm	0.30	0.70	1.81
Eu	Europium	0.23ppm	0.07	0.10	0.40
F	Fluorine	60.94ppm	20.99	25.00	143.00
Ga	Gallium	3.12ppm	1.06	1.10	7.50
Ge	Germanium	6.59ppm	6.71	1.00	43.00
Hf	Hafnium	0.45ppm	0.14	0.24	0.81
Hg	Mercury	0.20ppm	0.20	0.02	1.60
I	Iodine	2.0 ppm	1.2	< 1.0	5.8
In	Indium	0.02ppm	0.02	< 0.008	0.09
La	Lanthanum	6.9 ppm	2.2	3.3	12.
Lu	Lutetium	0.07ppm	0.02	0.041	0.11
Mn	Manganese	49.40ppm	40.15	6.00	181.00
Mo	Molybdenum	7.54ppm	5.96	1.00	30.00
Ni	Nickel	21.07ppm	12.35	3.00	80.00
P	Phosphorus	71.10ppm	72.81	5.00	400.00
Pb	Lead	34.78ppm	43.69	4.00	218.00
Rb	Rubidium	14. ppm	4.0	7.4	3.6
Sb	Antimony	1.26ppm	1.32	0.20	8.90
Sc	Scandium	2.4 ppm	0.57	1.4	3.6
Se	Selenium	2.08ppm	1.10	0.45	7.70
Sm	Samarium	1.1 ppm	0.62	0.4	3.8
Sn	Tin	4.79ppm	6.15	1.00	51.00
Sr	Strontium	37. ppm	20.	19.	130.
Ta	Tantalum	0.15ppm	0.05	0.10	0.30
Tb	Terbium	0.15ppm	0.06	0.04	0.24
Th	Thorium	2.01ppm	0.47	1.2	3.3
U	Uranium	1.6 ppm	1.1	0.5	4.5
V	Vanadium	32.71ppm	12.03	11.00	78.00
W	Tungsten	0.74ppm	0.56	0.04	2.1
Yb	Ytterbium	0.51ppm	0.13	0.31	0.77
Zu	Zinc	272.29ppm	694.23	6.00	5350.00
Zr	Zirconium	72.46ppm	57.78	8.00	133.00
*Al	Aluminium	1.29%	0.45	0.43	3.04
*Ca	Calcium	0.77%	0.55	0.05	2.67
Cl	Chlorine	0.14%	0.14	0.01	0.54
*Fe	Iron	1.92%	0.79	0.34	4.32
*K	Potassium	0.16%	0.06	0.02	0.43
*Mg	Magnesium	0.05%	0.04	0.01	0.25
*Na	Sodium	0.05%	0.04	0.005	0.20
*Si	Silicon	2.49%	0.80	0.58	6.09
*Ti	Titanium	0.07%	0.02	0.02	0.15

*These trace elements have high concentrations in coal, but they are major components of common rocks and soils and systematic toxicity to animals and humans has not been found, or is unknown.

Silicon (Si), aluminum (Al) and iron (Fe) are the predominant inorganic constituents of coal. They comprise 86% of the mineral matter. Calcium (Ca), sodium (Na), potassium (K), magnesium (Mg), chlorine (Cl), oxygen (O) and titanium (Ti) provide an additional 13.2%. These species are not classified as trace elements. The remaining inorganic elements provide less than 1% of the total mineral mass and are referred to as trace elements/6/. Trace elements can be bonded to either the organic or the mineral matter in coal. The type of association is dependent upon the properties and the physico-chemical processes the elements undergo, both during and after maturation of coal. Most trace elements have a partial organic and inorganic association. Mercury (Hg), zirconium (Zr), zinc (Zn), cadmium (Cd), arsenic (As), lead (Pb), molybdenum (Mo) and manganese (Mn) are generally bonded to the inorganic matter while germanium (Ge), beryllium (Be), boron (B) and gallium (Ga) are associated with the organic matter. The type of association has important consequences with respect to removing incombustible material prior to coal utilization. When coal is washed before combustion, those trace elements with the highest organic affinity remain with the clean coal, while those at the other extreme are washed away with the mineral matter/5/.

During combustion the trace elements are partitioned between the boiler slag and ash fractions (boiler ash, precipitator ash) which remain in the plant, and the ash (post precipitator ash) and gaseous species which escape to the atmosphere. Little is known about the series of chemical reactions/vaporization/condensation processes the trace elements undergo prior to their appearance in the various waste product fractions. The partitioning of trace elements between the various exit streams from the boiler and their eventual environmental impact is dependent upon a number of factors. These include (i) the chemical form of the elements in the coal; (ii) the concentration of the elements in coal; (iii) the combustion process, ie, type of boiler, firing temperature, load, etc; and (iv) flue gas emission control devices, eg, electrostatic precipitators, wet scrubbers. The sensitivity of the distribution of trace elements to these factors is the cause of the number of seemingly contradictory reports in the literature. Before results of different studies can be compared, these four factors must be considered/6/.

All ashes, regardless of their origin, are made up of spherical amorphous aluminosilicate particles with diameters ranging from less than 1 μm to 1000 μm /7/. The size distribution of the particles separates into two distinct modes, (i) a submicrometer mode containing particles approximately 0.1 μm in diameter and (ii) a "large" particle mode which includes particles with diameters greater than 0.5 μm . Particles in the size range 1-20 μm in diameter provide most of the mass of fly ash. As the combustion temperature increases, the amount of submicron particulate formed increases and the size distribution in the submicron mode becomes narrower. The mechanism for the formation of the submicron size particles is unclear. Electron microscopy studies by R.D. Smith et al/8/ suggest that particles below a few microns in diameter are much less heterogeneous than larger particles.

However, if all particles are formed via the same mechanism, one would expect no difference in the degree of heterogeneity between the different sized particles. Smith et al/8/ propose that the sub-micron sized particles are formed from the bursting of larger particles. The resultant large number of very small liquid particles coagulate to form single spherical particles in the 0.1 to 1.0 μm range. This process leads to the type of interparticle homogeneity suggested by the electron microscopy results. The bursting mechanism is supported by the physical characteristics of the larger fly ash particles. A large fraction of the particles in the 5-100 μm size range consist of either hollow spheres (cenospheres) or hollow spheres packed with a large number of smaller spheres (pleuospheres). The hollow spheres are believed to result from H_2O , CO_2 , and SO_2 evolution during rapid heating, which causes ballooning of the liquid particles. The smaller inner spheres are thought to result from an internal process also related to gas release. At temperatures slightly higher than those required for cenosphere formation, the viscosity of the liquid particles will be sufficiently small that the particles may burst, forming large numbers of droplets in the 0.1 μm size range. The bursting mechanism is further supported by the fact that sputtering experiments show that hollow particles are extremely rare in the smaller size fractions consistent with a different mechanism of formation than the larger particles/8/.

The aluminosilicate particles, no matter how formed, can serve as condensation nuclei for other volatilized species, ie, trace metals. Many reports in the literature/9/ suggest an inverse relationship between the aerosol trace element concentration and particle size. It is not, however, clear whether there is a d^{-1} or d^{-2} dependence (d = particle diameter). Most of the ash surface area is provided by submicron particles ($d \sim 0.03 \mu\text{m}$) even though these constitute only of the order of 1% of the total mass/9/.

Submicron particles resulting from the bursting-coagulation mechanism will have concentrations of volatilized elements determined by the relative amounts of condensation occurring before the bursting process, between bursting and coagulation, during coagulation and following the completion of coagulation. If all condensation occurs prior to the completion of coagulation, the concentration of the volatilized elements would be nearly independent of particle size in the size range dominated by the coagulation process. In general, finer ash particles, 1-10 μm diameter range, contain a higher concentration of the condensed elements because they have a larger surface area per unit mass compared to the coarser particles/8/.

Although the contribution of submicron size particles to the total fly ash mass is small, their impact on plant stack emissions can be significant. Coarse particles are filtered from the flue gas stream by particulate control devices, while the smaller particles generally escape to the atmosphere.

Trace elements can be divided into four categories on the basis of how they are partitioned in the waste products of coal combustion.

Elemental boiling point is not considered to be a major factor in influencing trace element separation. Group I consists of elements which are equally distributed in the fly ash and boiler slag; group II elements are generally concentrated on fly ash particles and relatively depleted in the bottom ash; group III species are completely volatilized and emitted from the stacks in the vapour phase; group IV elements show behaviour intermediate between groups I and II. Figure 1 illustrates the trace element members of each group and their position in the Periodic Table. Trace elements can also be classed according to the size of the fly ash particles on which they are preferentially adsorbed. Aluminum (Al), calcium (Ca), iron (Fe), potassium (K), lanthanum (La), magnesium (Mg), sodium (Na), scandium (Sc), strontium (Sr), thallium (Tl) and titanium (Ti) are found in relatively constant concentrations on particles greater than 1-2 μm in diameter. Their concentrations decrease rapidly on submicron particles. The more volatile elements, arsenic (As), bromine (Br), chlorine (Cl), copper (Cu), iodine (I), indium (In), antimony (Sb), selenium (Se) and tungsten (W) are preferentially concentrated on submicron size particles. Their concentrations increase as particle size decreases/10/. Barium (Ba), cobalt (Co), gallium (Ga), tantalum (Ta), uranium (U) and zinc (Zn), when emitted during coal combustion, also exhibit increasing concentrations as the particle size decreases. However, these elements fractionate quite differently depending upon their origin, ie, background versus anthropogenic/10/.

Most trace elements are volatile to some degree at the high temperatures encountered in the furnace ($\sim 1500^\circ\text{C}$). The majority of trace elements are thought to leave the boiler as the most stable high temperature oxide. A recent paper by W.D. Halstead/11/ reports that the preferred vapour phase form of the elements antimony (Sb), arsenic (As), germanium (Ge) and tin (Sn) is the oxide. AsO is the primary vapour phase species of arsenic at temperatures in the 1300-1500°C range. As the flue gases cool to below 700°C, As₂O₃ becomes predominant. In the case of cadmium (Cd), copper (Cu), lead (Pb), mercury (Hg), nickel (Ni), selenium (Se) and zinc (Zn), the chloride species are preferred. PbO is the predominant vapour phase form of lead at combustion temperatures; however, conversion to PbCl₂ is believed to occur below 900°C. Beryllium (Be) has been detected as Be(OH)₂ and molybdenum and chromium exist as the oxychloride. As the temperature of the flue gas decreases, condensation and deposition on the fly ash particles begin. Antimony (Sb), arsenic (As), beryllium (Be), copper (Cu), germanium (Ge), molybdenum (Mo), nickel (Ni), selenium (Se) and tin (Sn) are deposited as oxides. In the presence of SO₂, condensed phase chlorides are unstable and are converted to sulfates. As a result, cadmium (Cd), chromium (Cr), lead (Pb), mercury (Hg) and zinc (Zn) are deposited as sulfates. Conversely, vapour phase sulfates, except for those of alkali metals, are unstable. With continued cooling, the condensed oxides of antimony (Sb), beryllium (Be), nickel (Ni), copper (Cu) and tin (Sn) are converted to sulfates. Condensation generally occurs at temperatures less than 700°C. The temperature of the flue gas at the inlets to the air heater is 327°C, and at the electrostatic precipitator it is 147°C. The dew points of As, Pb, Cd and Se vary between 700-427°C. Since the ferroaluminosilicate particles solidify before cooling to 700°C, condensation of most of the trace metals occurs on the ash particles and there is no significant degree of

interaction between the ash and condensate. Exceptions are, however, beryllium (Be) and nickel (Ni) which condense at temperatures at which the aluminosilicate particles would still be fluid ($T > 900^{\circ}\text{C}$).

The amount of chlorine (Cl) initially present in coal can have a significant influence on the temperature at which condensation takes place. To illustrate, a decrease in the chlorine content of coal from 0.70 wt% (equivalent to a high Cl UK coal) to 0.01 wt% (as found in some US coals) could increase the flue gas dew point of lead by 160°C (eg, 667 to 827°C for 100 ppm Pb in coal)/11/. A list of the preferred species and dew points of some of the major trace inorganic elements in coal is given in Table II.

Elements existing in the gas phase as polar compounds, ie, metal oxides, can also adsorb on the ash and be collected with particulate metal oxides, sulfates, etc.

Mercury (Hg), a member of group 3, evaporates in the boiler and is too volatile to condense prior to the release of flue gases to the atmosphere.

Coal also contains many radioactive trace elements which are released during combustion. Fine particles which escape the electrostatic precipitator have been found to be very enriched, relative to coal, in ^{210}Pb , moderately enriched in ^{235}U and ^{238}U , and only slightly enriched in ^{226}Ra , ^{228}Ra and ^{228}Th . Gaseous radon is also discharged. In general, radioactive emissions from a coal-fired power plant are only a fraction of the ambient level/5/.

Tables of the average concentrations of trace inorganic elements in coal, bottom ash, precipitator ash, post precipitator ash and in the vapour phase of stack gas measured at Ontario Hydro's coal fired generating stations are provided in Appendices II-VI. As yet no data about the size distribution of the particles emitted from Ontario Hydro's power plants is available.

DEPOSITION

i) Dry Deposition and Dry Deposition Velocities

Dry deposition is the removal of particulates and gases from the atmosphere at the air-surface interface. The deposition velocity (V_d) is defined mathematically as the flux (F) (amount of material removed per unit time per unit area) divided by the average airborne concentration of the aerosol or gas (χ) (measured at a known height (Z_r), within the boundary layer above the surface)/12/.

$$V_d(\text{cm/s}) = \frac{F (\mu\text{g cm}^{-2} \text{s}^{-1})}{\chi (\mu\text{g cm}^{-3})}$$

Deposition velocities have been found to range over three orders of magnitude for particulates and over four orders of magnitude for gases. Dry deposition velocity is dependent upon a number of factors including particle size, wind speed, friction velocity, the nature of the receiving surface and the height above the surface at which the concentration measurement is made. Table III lists many other factors which affect

TABLE II
PREFERRED SPECIES AND DEW POINTS OF TRACE
ELEMENTS IN COAL-FIRED BOILER FLUE GASES/11/

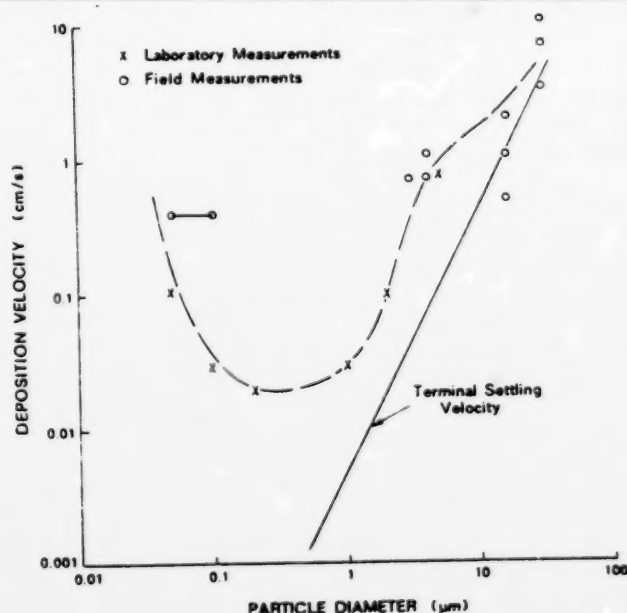
Element	Concentration Range in Coal ppm	Preferred Species at Dew Point		Dew-Point Range K
		Vapour Phase	Condensed Phase	
Antimony	1 - 10	Sb_4O_6	Sb_2O_3	890- 910
Arsenic	2 -100	As_4O_6	As_2O_3	810- 850
Beryllium	0.4 - 10	$\text{Be}(\text{OH})_2$	BeO	1230-1530
Cadmium	0.1 - 5	CdCl_2	CdSO_4	770- 830
Chromium	1 -100	CrO_2Cl_2	$\text{Cr}_2(\text{SO}_4)_3$	770- 840
Copper	10 - 50	Cu_3Cl_3	CuO/CuSO_4	800- 880
Germanium	1 - 20	GeO	GeO_2	1190-1270
Lead	10 -100	PbCl_2	PbSO_4	930- 980
Mercury	0.01- 10	HgCl_2	HgSO_4	290- 350
Molybdenum	1 - 10	MoO_2Cl_2	MoO_3	550- 690
Nickel	1 -100	NiCl_2	NiO	1250-1890
Selenium	1 - 10	SeCl_2	SeO_2	600- 660
Tin	1 - 10	SnO	SnO_2	1050-1110
Uranium	1 -100	UO_2	$\text{UO}_2/\text{U}_3\text{O}_8$	1840-2070
Zinc	30 -200	ZnCl_2	ZnSO_4	940-1000

TABLE III
SOME FACTORS INFLUENCING DRY DEPOSITION/13/

Micrometeorology Variables	Depositing Material		Surface Variables
	Particles	Gases	
Aerodynamic roughness:	Agglomeration	Chemical Activity	Accommodation:
Mass transfer	Diameter	Diffusion:	Exudates
a particles	Density	Brownian	Trichomes
b gases	Diffusion:	Eddy	Pubescence
Heat	Brownian	Partial pressure in equilibrium with surface solubility	Wax
Momentum	Eddy equal		Biotic surfaces
Atmospheric stability	a particle		Canopy growth:
Diffusion effect of:	b momentum		Dormant
Canopy	c heat		Expanding
Diurnal variation	Effect of canopy on diffusiophoresis		Senescent
Fetch			Canopy structure:
Flow separation:	Electrostatic effects:		Areal density
Above canopy	Attraction		Bark
Below canopy	Repulsion		Bole
Friction velocity	Gravitational settling		Leaves
Inversion layer	Hygroscopicity		Porosity
Pollutant concentration	Impaction		Reproductive structure
Relative humidity	Interception		Soils
Seasonal variation	Momentum		Stem
Solar radiation	Physical properties		Type
Surface heating	Resuspension		Electrostatic properties
Temperature	Shape		Leaf - vegetation:
Terrain:	Size		Boundary layer
Uniform	Solubility		Change at high winds
Non-uniform	Thermophoresis		Flutter
Turbulence			Stomatal resistance
Wind Velocity			Non-biotic surfaces
Zero-plane displacements:			pH effects on:
Mass transfer			Reaction
a particles			Solubility
b gases			Pollutant penetration and distribution in canopy
Heat			Prior deposition loading
Momentum			Water

dry deposition. The most important variable is particle size. In the absence of precipitation and assuming an altitude of 2 km, the calculated lifetime of particulates in the atmosphere (residence time) is 10-100 h for particles in the size range 1-10 μm and for particles less than 1 μm in diameter it is 10-1000 h/12/. The magnitude of dry deposition velocities is a function of Brownian and Eddy diffusion, and gravity settling. The smaller the particle size, the greater the Brownian diffusion coefficient and the nearer it approaches that for a gas. In the case of very small particles, those with diameters less than 0.1 μm , the deposition velocity is strictly a function of Brownian diffusion. Minimum deposition velocities are believed to occur for particles in the 0.1-1 μm size range. Only in this size range is V_d nearly constant for a selected roughness length, particle density and wind speed. Eddy diffusion is regarded as the important deposition process. Wind tunnel results indicate that deposition velocities for particles with diameters of 0.05-1 μm , and a wide range of wind speeds and for surfaces as different as short grass and forest, lie in the range $3 \times 10^{-3} - 5 \times 10^{-2} \text{ cm s}^{-1}$ /13/. Field observations for particles in this size range are difficult to perform and few are reported in the literature. Experimental results often suggest deposition velocities greater than 0.1 cm s^{-1} . In 1974 Cawse/12/ reported deposition velocities of submicron size trace element particulates, to filter paper, to be in the range $0.2-0.7 \text{ cm s}^{-1}$. In 1982, Garland/12/ reported deposition velocities to grass not exceeding 0.1 cm s^{-1} for particles in the 0.05-0.2 μm diameter size range. For particles larger than 1 μm diameter, the deposition velocity is accelerated by gravitational settling, the determining parameters being particle diameter (squared) and particle density/13/. Deposition velocities for particles with diameters greater than 10 μm are affected by the variability in wind speeds and friction velocities. Figure 2 illustrates the relationship between particle diameter and deposition velocity.

FIGURE 2
LABORATORY AND FIELD MEASUREMENTS OF
DEPOSITION VELOCITIES OF PARTICLES TO GRASS/15/



Dry deposition velocities for many materials and various deposition surfaces are given in Appendix I. The deposition velocities are listed as a function of particle diameter. Although no diameters are given for particles containing trace inorganic elements, the particles are assumed to be in the submicron size range/12/.

When measuring or calculating dry deposition velocities, the usual assumption is that the particles are solid spheres. However, in many cases the particle may not be spherical nor solid. As previously discussed, fly ash is made up of hollow spheres and aggregates of many smaller individual particles. Studies have shown that the settling velocities of aggregates can be as small as 0.01 of that for a solid particle of equal mass/13/.

ii) Wet Deposition

Wet deposition is the removal of pollutants by various types of precipitation, ie, rain, snow, etc. It consists of rainout (within cloud scavenging) and washout (below cloud scavenging) of particles or gases. Wet deposition can be considered to be an exponential decay process in which the atmospheric concentration of particles at time t (x_t) is expressed as the product of the atmospheric concentration of particles at time zero (x_0) and an exponential term involving the scavenging coefficient for particles ($\Lambda_p t$)/15/.

$$x_t = x_0 e^{-\Lambda_p t}$$

The scavenging coefficient is the concentration of particles in precipitation ($\mu\text{g/kg}$) divided by the concentration in air ($\mu\text{g/kg}$). Wet deposition is a complex process involving many variables, some of which include (i) droplet size distribution of the rain; (ii) particle size distribution of the aerosol; (iii) precipitation rate; and (iv) altitude of rain formation/16/.

The mechanism of the scavenging action is not clear. Removal of particulate matter appears to involve a combination of particle inertia, interception, electrostatic attraction, and random molecular (Brownian) motion/16/. Most metals tend to be concentrated about a thousand times more in precipitation than in air/14/. As in the case of dry deposition, particle size is important. Figure 3 illustrates the relationship between the rain scavenging rate and particle size. As can be seen from the graph, the more enriched trace elements in the atmosphere, those associated with submicron size particles and having higher volatilities, are less concentrated in precipitation than the larger particles/14/. Table IV lists field measurements of scavenging coefficients of particles. Work by E. Rohbock/17/ suggests that metals bound on submicron size aerosol particles are removed primarily by wet deposition, whereas metals bound on coarse particles are removed mainly by dry deposition. Trace elements in rain are not necessarily completely dissolved. Comparison of the insoluble fractions in both rain water and dry deposition samples suggests that the insoluble fraction in rainwater originates mainly from the washout of large atmospheric dust particles.

FIGURE 3

RELATIONSHIP BETWEEN RAIN SCAVENGING
RATES AND PARTICLE SIZE/15/

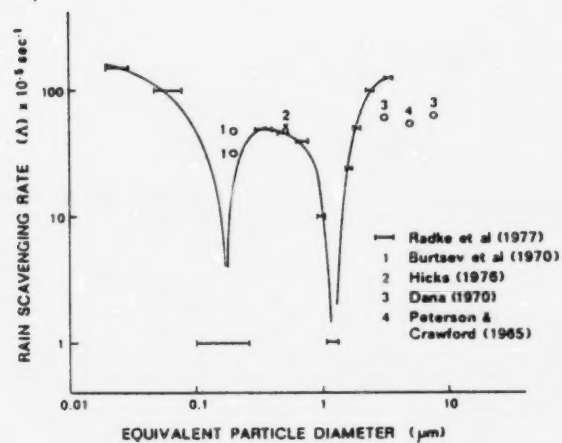


TABLE IV
FIELD MEASUREMENTS OF SCAVENGING
COEFFICIENTS OF PARTICLES/15/

Author (date)	Λ_p (s ⁻¹)	Particulate size (μ m)	Comment
Kalkstein <i>et al.</i> (1959)	2×10^{-5} 2×10^{-5}	SO ₂ , NH ₃ Cl, NO ₂	Rainout } Makhon'ko (1967) Washout }
Georgii (1963)	4×10^{-5} 22×10^{-5} 4×10^{-5}	} Dissolved inorganic contaminant	} Rainout Washout
Banerji and Chatterjee (1964)	0.4×10^{-5}		
Makhon'ko (1964)	2×10^{-5} $\leq 1 \times 10^{-5}$		
Shirvaikar <i>et al.</i> (1960)	7×10^{-5}	Atmospheric dust	Rainout Makhon'ko (1967)
Makhon'ko and Dmitrieva (1966)	20×10^{-5}	Fission products	Rainout
Makhon'ko (1967)	7×10^{-5}	Atmospheric dust	Rainout plus washout
Wolf and Dana (1969)	$0.5 \times 10^{-5} J$	0.5	Snow; Knutson and Stockham (1977)
Bakulin <i>et al.</i> (1970)	3×10^{-5}		²¹² Pb; washout from thunderstorm
Burtsev <i>et al.</i> (1970)	$15 \times 10^{-5} J^{0.5}$ $20 \times 10^{-5} J^{0.5}$	≈ 0.2 ≈ 0.2	Washout Rainout
Dana (1970)	$13 \times 10^{-5} J$	7.5, 3	Uranin and rhodamine particles respectively
Perkins <i>et al.</i> (1970)	300×10^{-5}	Atmospheric aerosol	Rainout
Peterson and Crawford (1970)	$16 \times 10^{-5} J^{0.8}$	5	Based on Engelmann's data (1965)
Esmen (1972)	0.4×10^{-5}	Atmospheric aerosol	Includes rainout
Rodhe and Grandell (1972)			Suggest Λ proportional to rainfall intensity
Acres-ESC (1974)	0.7×10^{-5}	Atmospheric aerosol	Includes rainout
Graedel and Franey (1975)	$\Lambda_{\text{new}} = 25-50\Lambda_{\text{old}}$	0.4-1	See Slinn (1976)
Hicks (1976)	50×10^{-5}	< 1	Rainout
Graedel and Franey (1977)	19×10^{-5} 18×10^{-5} 28×10^{-5} 43×10^{-5} 65×10^{-5} 92×10^{-5}	0.3-0.5 0.5-0.7 0.7-0.9 0.9-1.5 1.5-3	Condensation nuclei Snow

CONCLUSIONS AND RECOMMENDATIONS

The purpose of this report was to provide (i) information about trace inorganic element emissions from coal-fired power plants, and (ii) data with which to develop a trace inorganic element and particulate dispersion and deposition model (ie, particle size, dry deposition velocity, scavenging coefficient). Although many reports in the literature address these topics, the information provided is often contradictory and incomplete. The distribution of trace inorganic elements in the waste products of coal combustion is very dependent upon the type of coal burned and the firing conditions. As a result, almost all elements have been detected in all waste product fractions. Deposition velocities given for trace inorganic elements are often confusing in that the particle size is not clearly defined. It is recommended that for the purpose of development of a dispersion and deposition model only the size of the emitted particles be considered and not the identity of the elements adsorbed on them. The size of the particle determines its dispersion and rate of deposition, not the nature of the adsorbed species.

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APPENDIX I: Dry Deposition Velocities for Particles/13/

u = air velocity u_s = friction velocity v_i = monodispersed particle settling velocity

v_d = deposition velocity for a polydispersed aerosol determined in the field

Depositing material	Particle Size if Specified		Air Speed, cm s^{-1}		Atmospheric Stability	Deposition surface	Deposition velocity cm s^{-1}
	Diameter, μm	Other	u	u_s			
Particles	0.03-30			10-200		2, from	10^{-1} -40
Pollen	20	$v_i = 1.5 \text{ cm s}^{-1}$				Microscope slides in grassland	4.5(3xv _i) 9.9
Pollen	32-35 90-100 20	3.3 20 $v_i = 1.5 \text{ cm s}^{-1}$				Microscope slides in forest	60 1.5(1xv _i) 3.3
Lycopodium spores	32-35	3.3				Glass plate	20
Lycopodium spores	90-100	20				Grassland	0.7-3.5 0.7-3.5
Lycopodium spores	32	$v_i = 1.4$ - 2.1 cm s^{-1}	110-920 104-740	12-94		Moss bags Moss bags pine and oak shoots	9x(grass v _d) 15x(grass v _d) 0.003-10
Oleic acid	0.5		10^2 - 10^3				0.02-30 0.1-60
Uranine	2					Tray	7.3
Plutonium	5 10					Snow	3.2 <0.6-19
Rhodamine B	0.8					Snow	0-34
ZnS	5 MMD	0.3 MMD				Sagebrush	1.5-3.4
ZnS	5	16-29 MMD				Paper	0.005-0.06
CuSO ₄	3-7			8-34		Smooth metal	0.007-0.08
						Rough metal	0.006-0.007
						Grass	0.015-0.15
						Clover	0.018-0.15
						Soil	0.01-0.05
ZnCdS	3	$v_i = 0.13 \text{ cm s}^{-1}$				Artificial surface in forest	0.1-0.5
Natural aerosol blowing field	2-5 1-10		600		Stable	Sagebrush	0.5
Plutonium		<6m, most $\approx 1 \mu\text{m}$ 1-2 MMD	0.4			Grass sward	0.8 9.8
Pu(NO ₃) ₄		0.5-1.7	1			Leaf area	4×10^{-1} 8×10^{-1}
						Single bean leaf	2.6×10^{-1} 2.7×10^{-1}

APPENDIX I (Continued)

Depositing material	Particle size if specified		Air speed, cm s ⁻¹		Atmospheric stability	Deposition surface	Deposition velocity cm s ⁻¹
	Diameter, μ m	Other	u	u _a			
Pu compounds		0.8-1.8	1			Plant canopy	3.5x10 ⁻⁴
Uranine	<1					Sand	1.2x10 ⁻⁴
7Be	<1					Ocean with rain	0.03-0.3
Au colloid Particles	0.8					Bean leaf	<0.06-5.3
	0.05-0.1			5.5-20		Field	4x10 ⁻⁴
Beta-gamma Kiwi effluent	Median	ug				Resin coated tray at 0.8 m height at distance, m	Increases with u _a 0.1-1.1
	0.003-0.6					4900	0.4-0.8
	0.006	16				9800	2-85
	0.1	8				39,000	0.1-3
	0.1-0.4					1220	0.2-0.4
	0.6	4				1220	0.07-0.50
	0.2-1.4					2440	0.08-110
	0.02-0.2					9800	0.3
	0.02-4					1220	0.4-2.5
	0.4-6					610	7-110
	0.1-8					1220	0.9-100
	2.8	4				4900	0.3-3
	2.7-6					2440	0.4-5
	3.9	3				2440	0.03-3
	2.3-4					1220	0.5-6
	5	4				4900	48-180
Pb auto exhaust	Aggregated					Whole leaves	0.008-0.12
	Aggregated exhaust-0.04-0.01					Leaf discs	0.001-0.17
	Non-aggregated (Aggregated)					Moss bags	0.1-2
						Bare soil	0.005-0.05
						Filter paper	0.003-0.1
						Moss bags near highway	0.7-39
						Grass	0.13 (0.019)
						Soil under grass	0.015 (0.007)
						Bare soil	0.035 (0.008)

APPENDIX I (Continued)

Depositing material	Particle size if specified		Air speed, cm s ⁻¹	Atmospheric Stability	Deposition Surface	Deposition Velocity cm s ⁻¹
	Diameter, μ m	Other	u			
Trace elements					Grass & Soil	0.14 (0.026) <0.4-1
					Filter paper at 1.5 m	0.05-4.8 <0.01->3 0.06-13
Trace elements					Filter paper at 1.5m	0.2-4.3 0.6->3 0.9-2.7 0.2-6.3 0.6-13 0.4-1.4 0.6-2.5 0.7-2.2 0.2-<0.7 0.6-6.8 0.4-0.9 1.0-2.5 0.3-1.9 0.7-<2 <0.6-1.1 0.4-4.5 <0.1-<0.6 0.1-0.6 0.1-2.6 <0.9-3.0 <0.3-1.1 <0.4->8 0.3->6 0.06-<0.4 <0.3-<2 0.2-0.6 >0.6-3.5 0.5-1.9 0.6-4.1 0.3->2 0.7-2.2 0.2-6.4
					Open bucket	
Trace elements						
Na						
Mg						
Al						
Cl						
K						
Ca						
Sc						
Ti						
V						
Cr						
Mn						
Fe						
Co						
Ni						
Cu						
Zn						
As						
Se						
Br						
Rb						
Ag						
Cd						
In						
Sb						
I						
Cs						
La						
Ce						
Sm						
Eu						
Th						

APPENDIX I (Continued)

Depositing material	Particle size if specified Diameter, μm	Air speed, cm s^{-1} u	Atmospheric stability	Deposition surface	Deposition velocity cm s^{-1}
Cl					6.4
K					2.6
Ca					2.6
Br					2.3
Fe					0.37
Mn					0.59
Ti					0.67
Pb					0.60
Se					0.38
As					0.24
V					0.70
Cu					0.24
Ni					3.0
Zn					4.0
^7Be					1.8
RaB and RaC				Filter Paper	0.96
Field tests					0.05
^{137}Cs		Deposition Independent increases of lapse with u			
^{103}Ru				Water	0.0910.06
				Soil	0.0410.05
				Grass	0.2-0.5
				Sticky paper	0.2-0.4
				Water	2.311.0
				Soil	0.110.2-
					<0.610.4
$^{95}\text{Zr}-^{95}\text{Nb}$				Grass	0.02-0.8
				Sticky paper	0.2-2.011.0
				Water	5.713.4
				Soil	2.912.7
				Sticky paper	1.410.7
^{141}Ce				Sticky paper	0.710.6
^{127}Te				Sticky paper	0.710.6
Pb, auto exhaust				Sticky paper	0.711.3
Pb		Light Stable		Teflon	0.29
				Snow	0.16-2.0

APPENDIX 1 (Continued)

Depositing material	Particle size if specified Diameter, μm	Air speed, cm s^{-1} u	Atmospheric stability	Deposition surface	Deposition velocity cm s^{-1}
Sulfate Fission products		Light	Stable	Snow Desert vegetation	0.2-2.9
Fluorides				Forage Vertical lined	0.310-0.02 0.4910.19
Beta activity Mixed fission products (MFP)				filter paper Sticky plate Grass	1.0 0.04-0.3
				Grass substrate Filter paper Grass Substrate Grass Substrate Oats Ears Stalks Water	0.02-0.17 0.03-0.16 0.001-0.003 0.001-0.006 0.002-0.004 0.003-0.01 0.001-1.2 0.004-1.8 Function of particle diameter
Ua					
Sr					
MFP, Ua, Sr					
Pb Atmospheric fallout				Water Pluimeter Fallout collectors Annual Monthly Sticky paper Tank	Function of particle diameter and u 0.13 0.05-0.9 0.2-3.4 0.07 0.05-0.5
Atmospheric fallout					
RaD					
Natural aerosol lead, bromine, zinc				Great Lakes Urban St Louis 1973 1975	0.8-7.6 2.211.4 1.810.7

APPENDIX 11

CONCENTRATION RANGES OF ELEMENTS IN COAL/3/

Concentration Range (mg/kg)

	1	1 - 10	10 - 100	100 - 1000	1000 - 10 000	> 10 000					
Sb	0.50	Co	3.3	As	12.4	Ba	147	Ca	3958	Al	11 040
Be	0.88	Cu	5.8	B	16	Mg	417	Cl	1174		
Cd	0.27	Dy	1.0	Br	14	Na	506	Fe	6377		
Cs	0.8	Ga	9.5	Cr	12	Sr	118	K	1233		
Eu	0.3	I	1.1	F	77	Ti	555				
Hf	0.7	La	4.8	Mn	24						
Lu	0.2	Pb	6.0	Rb	13						
Hg	0.35	Ni	4.0	V	20						
Ta	0.3	Sm	1.0	Zn	27						
Th	0.3	Sc	3.1								
U	0.7	Se	2.70								
Yb	0.4	Ag	1.7								
		Th	1.4								

CONCENTRATION RANGES OF ELEMENTS IN BOTTOM ASH/3/

- 23 -

CONCENTRATION RANGES OF ELEMENTS IN PRECIPITATOR ASH/3/

- 24 -

APPENDIX V

CONCENTRATION RANGES OF ELEMENTS IN POST-PRECIPITATOR ASH/3/

Concentration Range (mg/kg)

< 1		1 - 10		10 - 100		100 - 1000		1000 - 10 000		> 10 000	
I	NIL	Cd	4.3	Sb	11.2	As	233	Ba	1540	Al	103 000
Lu	0.6	Cs	6.1	Be	10	Cl	790	B	1900	Ca	20 700
Hg	0.5	Dy	5.0	Br	29	Cr	216	Mg	4380	Fe	69 900
Tb	0.8	Eu	2.5	Co	36	Cu	142	Na	3410	K	11 000
.		Hf	3.3	La	52	F	449	Ti	5850		
		Sm	9.4	Rb	86	Ga	138				
		Ag	7.5	Sc	22	Pb	158				
		Ta	1.0	Th	10	Mn	254				
		U	7.8			Ni	193				
		Yb	2.8			Se	261				
						Sr	970				
						V	239				
						Zn	375				

APPENDIX VI

CONCENTRATION RANGES OF ELEMENTS IN THE VAPOUR PHASE OF STACK GAS/3/

Concentration Range ($\mu\text{g}/\text{m}^3$ at 25°C and 101.3 kPa)

	1 - 10	10 - 100	100 - 1000	1000 - 10 000	> 10 000
Be	NIL	Al	B	Br	Cl
Cs	0.2	Ba	Ca	F	82 260
Dy	0.1	Cr	I		
Eu	NIL	Fe	K		
Ga	NIL	Mg			
Hf	0.3	Mn			
La	NIL	Hg			
Lu	0.1	Ni			
Rb	0.2	Na			
Sm	0.2	Sr			
Sc	NIL	Ti			
Ta	0.2	Zn			
Tb	0.2				
Th	0.2				
U	0.1				
V	0.4				
Yb	0.1				

POOR

QUALITY

ORIGINAL